



Zr/P/O catalyst for the direct acid chemo-hydrolysis of non-pretreated microcrystalline cellulose and softwood sawdust

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ABSTRACT

This paper compares the catalytic behavior of several heterogeneous acid catalysts in the direct hydrolysis of an untreated softwood dust. Among the various catalysts investigated, some were characterized by a relatively high yield to monosaccharides, such as a Zirconium phosphate and the reference Amberlyst 15. Conversely, some catalyst types, i.e. Sn/W mixed oxide and Zirconia-grafted trifluoromethanesulfonic acid, were selective into glucose, since sugars derived from hemicellulose dissolution and hydrolysis were rapidly degraded. A detailed analysis of the reactivity of Zr/P/O was conducted, in the hydrolysis of both untreated and ball-milled microcrystalline cellulose; at 150 °C and 3 h reaction time, the catalyst gave high selectivity to glucose, with negligible formation of 5-hydroxymethylfurfural, and moderate cellulose conversion. After cellulose ball-milling, a notable increase in conversion was achieved, still with a high selectivity to glucose and very low formation of degradation compounds. The catalyst showed high affinity for β-1,4-glucans, as demonstrated by the activity in cellobiose hydrolysis into glucose.

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1. Introduction

The conversion of lignocellulosic biomass into valuable chemicals is a strategic issue within the framework of the biorefinery concept, the aim of which is to develop a biomass-derived platform while avoiding competition with renewable resources focusing on satisfying food demand [1–16]. The starting point of the transformation chain is the deconstruction of the lignocellulosic biomass and depolymerization of the hemicellulose and cellulose, with the aim of either preserving the integrity of monosaccharides–structural components of these natural polymers–for further enzymatic transformations, or even directly transforming sugars into other valuable bio-based building blocks. Difficulties derive from both the resistant lignin sheath protecting the rigid structure made of hemicelluloses and cellulose microfibrils against chemical and physical degradation, and the tight

packing of cellulose chains, which protects the β-1,4-glycosidic linkages between monomeric units from water penetration.

Because of this, pretreatments are needed, for instance by means of harsh hydrolysis conditions (high temperature and therefore high pressure) [17–24]. Indeed, the hydrolysis of cellulose with diluted or concentrated HCl and H₂SO₄ has been used for a long time. Drawbacks of approaches using mineral acids for pretreatment include corrosion problems (especially when concentrated acids are used) and the need for both a neutralization step with significant salt formation, and downstream purification. Solutions aimed at avoiding these problems include: (a) the use of water-soluble organic acids which can be recovered by means of solvent extraction and recycled to the pre-hydrolysis step; and (b) the use of solid acids, which should be easily separated from residual solids [25–29]. Other approaches include the use of microorganisms, such as bacteria which can produce enzymes able to hydrolyze cellulose to glucose; in this case, drawbacks include the cost, an often low productivity, and poor flexibility with regard to the several types of raw materials.

For these reasons, there is a great interest in developing solid acid catalysts which are effective in cellulose hydrolysis; potential advantages would be the easier separation of the solid catalyst from

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the hydrolysate, an absence of corrosion phenomena, and a lower cost for product purification. Ideally, the solid catalyst should be easily recoverable and reusable. Bifunctional approaches have also been reported, in which the hydrolysis is combined with hydrogenation (hydrolytic hydrogenation), in the presence of H₂ and noble metals or transition metal catalysts, with the aim of in situ generating high concentrations of mobile protons, and hydrogenate sugars into sugar alcohols [30–41]. The use of ionic liquids, in synergy with the acidic catalyst, can also help in achieving efficient cellulose hydrolysis, under mild conditions [42].

Although some recently described soluble acids, especially those based on polyoxometalates, turned out to be very active in cellulose depolymerization and highly selective to glucose formation, most scientific efforts have gone in the direction of implementing solid acid catalysts for converting cellulose, either as such or after pretreatment. Typical conditions used include temperatures lower than 200 °C, with the aim of limiting both glucose decomposition and catalyst decomposition; the latter is a problem sometimes encountered with sulfonated organic resins and, in general, with catalysts in which the active species is based on sulfate groups (such as sulfonated activated carbon, carbon-silica nanocomposites, and SBA-15), which nowadays are considered the most efficient solid systems for cellulose hydrolysis [43–52]. Highly efficient catalysts also made for the hydrolysis of pre-treated cellulose are based on Ru on mesoporous carbon CMK-3 [53–55].

Another key issue in achieving highly efficient systems is the interaction between the cellulosic substrate and the active surface area of the solid catalyst; in this regard, the best results achieved so far make use of functionalized mesoporous carbon materials, whose polar surfaces allow adsorption of β-1,4-glucans, combined with high acid strength, high density, and water tolerance of sulfate groups in sulfonated materials [25–29,34]. Ball-milling pretreatment, an energy-intensive operation, is extensively used with the aim of decreasing the crystallinity of cellulose. Indeed, the main challenge in cellulose hydrolysis remains the degradation of crystalline domains; in fact, depending on the cellulose crystallinity, a limited conversion is usually reached (the so-called leveling-off degree of polymerization).

In this context, a solid catalyst which might facilitate hydrolysis while avoiding energy-intensive pretreatments for the biomass, using reasonable catalyst-to-biomass ratio, and which can be recovered from the solid residue, would represent a considerable step forward toward the goal of developing a sustainable process for lignocellulose conversion. In this paper, first we compare various solid acid catalysts in the direct chemo-catalytic hydrolysis of an untreated softwood dust, and then we describe an easy-to-prepare catalyst based on Zr hydrogen phosphate, which shows good performance in the direct hydrolysis of the wood, as well as excellent performance in the hydrolysis of both untreated crystalline cellulose and cellobiose.

2. Experimental

2.1. Preparation of catalysts

Zirconium Phosphate. Zr/P/O was prepared as indicated by Kamiya et al. [56], by the precipitation of ZrOCl₂ 8H₂O (32 mL of 1 M solution) and NH₄H₂PO₄ (64 mL of 1 M solution), at a molar ratio of P/Zr = 2. The precipitate was filtered, washed with water, and dried at 100 °C; before reaction it was calcined at 400 °C for 3 h.

Sulfonated-Zirconium Phosphate. Sulf-Zr/P/O was prepared by suspending Zr/P/O in H₂SO₄ 96 wt%; the slurry was dried at 100 °C, and calcined at 400 °C for 3 h [57].

Silica-Zirconia cogel. Si/Zr/O was prepared by dissolving 21 g of Tetraethylorthosilicate (TEOS) in 100 mL ethanol 99 wt%; then 4.25 g of Zirconium propoxide and 5 g of polystyrene powder were added slowly and under vigorous stirring. Afterwards, 11 mL of 1 M aqueous solution of tetrapropylammonium hydroxide (TPAOH) and 9 mL of water were added rapidly. The gelation occurred in 1.5 h. The solid obtained was dried at 100 °C under vacuum and calcined in static air at 550 °C for 6 h (rate 0.5 °C/min) [58,59].

Sulfated Silica-Zirconia. Sulf-Si/Zr/O was prepared by impregnating Si/Zr/O with a 1.8 M solution of (NH₄)₂SO₄ dried at 110 °C and calcined at 650 °C for 3 h [60].

Nafion® incorporated in SiO₂. Nafion-SiO₂ was prepared by dissolving 18 g of Si(OMe)₄ in 3 g of deionized water, containing 0.26 mL of 0.04 M HCl; the solution was stirred for 45 min to give a clear solution. 13 g of CaCO₃ and 13 mL of 0.4 M NaOH solution were then added to 26 mL of a Nafion® resin solution (which contains 5 wt% of Nafion® resin), while stirring. The NaOH solution was added over 15 min. The silicon-containing solution, prepared as described above, was added rapidly to the stirred Nafion®/NaOH-containing solution. Within about 10–20 s, the solution gelled. The solid gel was dried at about 95 °C for about two days, and then dried under vacuum overnight (95 °C). The resulting composite was re-acidified by stirring in a 3.5 M HCl solution and subsequently washed with deionized water. This process was repeated four times. The material was then treated with 25 wt% HNO₃ at 75 °C for 10 h. Lastly, the product was dried at 100 °C for 24 h [61].

Trifluoromethanesulfonic acid grafted on Zirconia. TFA-ZrO₂ was prepared by dissolving zirconium propoxide 70 wt% (34 g) in 118 g of 2-methyl-1-propanol; the solution was held at 90 °C and stirred for 10 min. Then 3 mL of deionized water was added drop-wise into the mixture under stirring. After 30 min of stirring, a solution of the desired amount of Trifluoromethanesulfonic acid in dichloromethane was slowly added to the above mixture and stirring continued for 2 h. The mixture was cooled, filtered, washed with deionized water and acetone, and then dried at 100 °C for 6 h. A Soxhlet extraction was carried out for 24 h using a mixture 50:50 v/v of dichloromethane and diethyl ether. The sample was dried at 200 °C for 10 h [62].

Sn-W Mixed Oxide. Sn/W/O was prepared by dissolving Na₂WO₄2H₂O (2.47 g) in deionized water (15 mL); then SnCl₄5H₂O (5.26 g) was added in a single dose; the Sn/W molar ratio was 2.0. After the solution had been stirred for 1 h at room temperature, deionized water (60 mL) was added in a single step and the colorless solution gradually became a white slurry. After the latter had been stirred for 24 h at room temperature, the resulting white precipitate of Sn/W hydroxide was filtered off, washed with a large quantity of deionized water (2 L), and dried under a vacuum. The solid was calcined at 800 °C for 3 h in an air atmosphere [63].

Amberlyst 15 (supplier Sigma–Aldrich) was also used as a reference sulfonated system.

High energy ball milling of cellulose was carried out using a SPEX CertiPrep 8000-series Mixer/Mill, using vials with tungsten carbide-lined body and two 7/16 in. tungsten carbide spheres.

2.2. Reactivity experiments

The hydrolysis of biomass was conducted in a stainless Teflon®-lined autoclave at 150 °C under autogenic pressure. The biomass was dried overnight before use at 80 °C under vacuum. In a typical run, 2.5 g of dried lignocellulose (or microcrystalline cellulose), 2.5 g of catalyst, and 50 g of water were introduced into the vessel; the reaction was carried out at 150 °C for 5 h. Afterwards both the unreacted biomass and the catalyst were separated from the aqueous solution by filtration; the residue was dried overnight at 80 °C under a vacuum, and then weighed. The solution was analyzed with a Dionex ICS1100 ion chromatograph equipped

with a DionexCarboPac PA20 anion-exchange column and a Pulsed Amperometric Detector ED50, to identify and quantify the monosaccharides. The solution was also analyzed with an Agilent 1260 Infinity HPLC equipped with DAD-UV detector and an Agilent Poroshell 120 EC-C18 (2.7 μ m, 4.6 \times 50 mm 699975-902) column for the quantification of the byproducts (5-hydroxymethylfurfural, furfural, levulinic acid).

Catalytic performances were expressed similarly to what had been done by Marzialetti et al. [64]. The conversion of biomass (X) was expressed as total mass dissolved during the process (Eq. (1)); the relative error on biomass conversion, calculated from repeated experiments, was equal to $\pm 10\%$. Weight yields (Y) to monosaccharides and byproducts (hydroxymethylfurfural HMF, furfural F and levulinic acid LA) were expressed as follows (Eqs. (2) and (3)):

$$X_{\text{lignocellulose}} = \frac{m_{\text{lignocellulose}} - m_{\text{residue}}}{m_{\text{lignocellulose}}} \quad (1)$$

$$Y_{\text{totMonosaccharides}} = \frac{m_{\text{monosaccharides}}}{m_{\text{lignocellulose}}} \quad (2)$$

$$Y_{\text{HMF+F+LA}} = \frac{m_{\text{HMF}} + m_{\text{F}} + m_{\text{LA}}}{m_{\text{lignocellulose}}} \quad (3)$$

Weight yield to oligomers was determined by mass balance, as the difference between the converted biomass and the sum of yields to monosaccharides and decomposition products. This method is not rigorous, since it assumes that no other byproducts are formed. Indeed, this latter assumption was valid as long as the hydrolysate, after filtration of the residual solid, was clear and therefore did not contain any further brownish degradation compounds (e.g. humins). In general, this was true during the first 5–6 h reaction time for experiments carried out at 150 °C, with all catalysts tested, whereas it was no longer valid both for longer experiments and in experiments carried out at 200 °C.

Moreover, since a softwood sawdust was used as the starting biomass, it is possible to distinguish monosaccharides coming from either cellulose ($m_{\text{mono-cell}}$) or hemicellulose ($m_{\text{mono-hemi}}$); by using the Eqs. (4) and (5) it is possible to express the yield by mass of monosaccharides coming from cellulose ($Y_{\text{mono-cell}}$) and hemicellulose ($Y_{\text{mono-hemi}}$), respectively. The equations giving $m_{\text{mono-cell}}$ (Eq. (6)) and $m_{\text{mono-hemi}}$ (Eq. (7)) have been derived taking into account that the main type of hemicellulose present in softwoods is galactoglucomannan, which is made of glucose, galactose, and mannose in several compositions. The equation has then been derived considering the presence of a galactoglucomannan of mean composition, with a ratio between main sugars comprised between galactose/glucose/mannose = 1/1/3 and 0.1/1/4.

$$Y_{\text{mono-cell}} = \frac{m_{\text{mono-cell}}}{m_{\text{lignocellulosa}}} \quad (4)$$

$$Y_{\text{mono-hemi}} = \frac{m_{\text{mono-hemi}}}{m_{\text{lignocellulosa}}} \quad (5)$$

where:

$$m_{\text{mono-cell}} = m_{\text{Glucose}} - 0,28m_{\text{Mannose}} \quad (6)$$

$$m_{\text{mono-hemi}} = 1,28m_{\text{Mannose}} + m_{\text{Arabinose}} + m_{\text{Galactose}} + m_{\text{Xylose}} \quad (7)$$

The average composition of the coniferous softwood used for hydrolysis experiments was: 65% polyglycosides (45% cellulose, 20% hemicellulose), 30% lignin, 5% others (extractable, resins, ash).

2.3. Characterization of catalysts

Ammonia-TPD characterization was carried out on selected samples in order to determine the acidity; the instrument was a

Thermoquest TPDR 1100. Samples were pretreated at 400 °C in He flow to remove contaminants. Then pulses of NH₃ (10% in He) were fed at 110 °C on the sample, until saturation was reached. Then the sample was heated (heating rate 10 °C/min) from room temperature to 600 °C, and the desorption of ammonia was recorded by means of a TC detector.

The quantitative analysis of P and Zr, both in catalyst and in the hydrolizate, was carried out by means of XRF (Panalytical Axios Advanced instrument).

3. Results and discussion

3.1. The direct hydrolysis of conifer wood (softwood sawdust)

Diluted-acid pretreatment of biomasses is typically carried out with sulfuric acid, and is mainly aimed at removing the hemicellulose fraction; in fact, the removal of hemicellulose increases the digestibility of the cellulose in the residual solid [11,16,64–66]. Acid hydrolysis of several biomass sources has been reported in literature; these include agricultural residues (such as corn stover and switchgrass) and wood, both hardwoods and softwoods. For example, in the diluted sulfuric acid hydrolysis of a softwood species [64], aimed at the selective hydrolysis of the hemicelluloses fraction, nearly complete selectivity was achieved at 150 °C, pH 1.65 for 1 h, without a significant dissolution of the cellulose. 70% yield to xylose (referred to the hemicellulose fraction) is obtained from softwood chips in a few minutes' reaction time and at a temperature of 190 °C, with 0.7% sulfuric acid concentration [67]. The pretreatment can even be preliminary to a high-temperature acid hydrolysis of the residual cellulose. However, the treatment with the diluted acid of the biomass may also be aimed at reducing the crystallinity of the cellulose, increasing cellulose porosity, and improving hydrolytic enzyme accessibility to cellulose fibers, in combination with hemicellulose removal. A further hydrolysis of cellulose to oligosaccharides and glucose can be carried out; in this case also, the further breakdown of glucose to HMF and even to levulinic acid may occur. Cellulose hydrolysis can be carried out either with concentrated H₂SO₄ or HCl (Bergius process), at room temperature, or using diluted acids at high temperature, when the aim is to maximize the sugar yield. In the two-step saccharification of wood, acid hydrolysis with concentrated sulfuric acid is first carried out at low temperature and with a short reaction time, a step aimed at producing oligosaccharides, whereas a second step is carried out with diluted sulfuric acid at a higher temperature, for hydrolysis into monosaccharides. Lastly, acid hydrolysis is also used for the manufacture of furfural, since the xyloses produced by xylan hydrolysis may be further transformed into furfural by acid catalysis.

The main parameters in acid hydrolysis are time, temperature, acid-to-biomass ratio, and water-to-biomass ratio. We carried out hydrolytic experiments using several solid acid catalysts (see Section 2.1 for a detailed description of catalyst preparation). Table 1 shows the comparison for all the catalysts used, showing the values of biomass conversion, total yield to monosaccharides, yield to sugars from cellulose hydrolysis, yield to decomposition compounds (furfural F, 5-hydroxymethylfurfural HMF and levulinic acid LA), and yield to oligomers. Catalysts showed notable differences in performance; more specifically:

The most active catalysts were TFA-ZrO₂ and Nafion-SiO₂, but the greatest yield to monosaccharides was obtained with Zr/P/O, sulf-Zr/P/O and Amberlyst 15. This indicates that these latter catalysts have a great affinity for glucans and xylans, and develop an efficient interaction with oligomers, thus allowing an efficient transformation of the latter into monosaccharides.

For Sn/W/O and TFA-ZrO₂, the yield to sugars from cellulose was equal to the overall yield to monosaccharides; in fact the only

Table 1

Catalytic behavior of various heterogeneous systems studied.

Catalyst	Biomass conversion (%) ^a	Y total monosaccharides (wt%)	Y cell; hemicell monosaccharides (wt%) ^b	Y HMF + F + LA (wt%)	Y oligomers (wt%)
Autohydrolysis	23 ± 3	1.9	0; 1.9	4.7	16
Zr/P/O	40 ± 4	12.9	1.7; 11.2	30.3	0
Sulf-Zr/P/O	42 ± 4	16.5	2.9; 13.6	30	0
TFA-ZrO ₂	53 ± 4	5.5	4.7; 0.8	10.5	37
Si/Zr/O	34 ± 4	0.8	0; 0.8	8.2	25
Sulf-Si/Zr/O	38 ± 4	6.9	0.5; 6.4	21.3	10
Nafion-SiO ₂	46 ± 4	6.8	0.2; 6.6	7.5	32
Sn/W/O	38 ± 4	4.1	4.1; 0	2.7	31
Amberlyst 15	34 ± 4	9.4	3.2; 6.2	20	0
Dil. H ₂ SO ₄ ^c	36	18.7	2.0; 16.7	2.7	14

^a Conversion and yields were calculated referring to the initial total weight of the dry biomass, not to the weight of hemicelluloses + cellulose contained in the biomass.^b Y cell monosaccharides: yield to monosaccharides from cellulose hydrolysis; Y hemicell monosaccharides: yield to monosaccharides from hemicelluloses hydrolysis.

Reaction conditions: 2.5 g untreated softwood, 2.5 g catalyst, 50 mL water, T 150 °C, reaction time 5 h.

^c Reaction conditions: T 166 °C, reaction time 0.5 h, pH 1.4, 0.4 wt% H₂SO₄.

sugar present after 5 h reaction time was glucose: xylose and other monosaccharides had been completely converted into degradation compounds.

Oligomers were the prevailing products with TFA-ZrO₂, Si/Zr/O, Nafion-SiO₂, and Sn/W/O. With a few catalysts, the yield to oligomers was negligible: Zr/P/O, sulf-Zr/P/O and Amberlyst 15. However, the latter systems were also those showing the greatest formation of decomposition compounds (especially furfural).

As mentioned above, degradation compounds were the prevailing products with Zr/P/O, sulf-Zr/P/O, and sulf-Si/Zr/O. With all solid catalysts however, the yield to degradation compounds was greater than that of monosaccharides, the only exception being the Sn/W/O system.

3.2. A more detailed study of the Zr/P/O system

Table 1 also shows the yields obtained with diluted sulfuric acid, under optimal conditions as reported in the literature. It can be seen that the main difference between the heterogeneous Zr/P/O system and the homogeneous catalyst concerned both the yield to degradation compounds (which was notably higher with the former catalyst) and the yield to oligomers. Conversely, there was a minor difference between the two catalysts as far as both total yield to monosaccharides and yield to glucose from cellulose are concerned.

Because of the relatively high yield to monosaccharides obtained, the good biomass conversion, the negligible formation of oligomers, and the similarity with the Amberlyst 15 reference catalyst, we focused on the Zr/P/O system, conducting a more detailed investigation of the catalytic behavior. The Zr/P/O system is described as a water-tolerant catalyst, which is active in acid-catalyzed reactions carried out in aqueous medium [47]. It is worth noting that Zr phosphate was also described as a catalyst providing the acidic functionality in a bifunctional Ru-Zr/P/O system for the hydrodeoxygenation of aqueous sugar solutions obtained by the hydrolysis of maple wood in a recent paper by Li et al. [68].

The Zr/P/O catalyst used was amorphous, and showed a surface area of 108 m²/g, and P/Zr atomic ratio (as determined by XRF) equal to 1.9 ± 0.1; this corresponds to the hypothetical formula of the compound Zr(HPO₄)₂. The acidity, as determined by NH₃-TPD, highlighted a considerable acid strength, with the maximum ammonia desorption peak at 350 °C, the desorption being completed at 550 °C; surprisingly, the desorption profile turned out to be very similar to that of a commercial H-Y zeolite having SAR equal to 6.

Fig. 1 (top) and 2 (top) show the effect of reaction time on biomass conversion, overall yield to monosaccharides, yield to sugars from the cellulose fraction, and yield to degradation com-

pounds, for the Zr/P/O and the Amberlyst 15 catalysts (worthy of note, all values were calculated with respect to the total dry biomass weight, not to the polyglycoside fraction only). The corresponding bottom figures show the details for monosaccharides and degradation compounds.

The maximum conversion achieved under the given conditions with the Zr/P/O catalyst (**Fig. 1**) was 40%; given the amount of polyglycosides in the biomass, it is apparent that only 70% of the hydrolyzable fraction was dissolved and hydrolyzed. For short reaction times, prevailing products were the oligomers obtained by the dissolution of the hemicellulose, whereas the initial formation (nil reaction time) of degradation compounds and monosaccha-

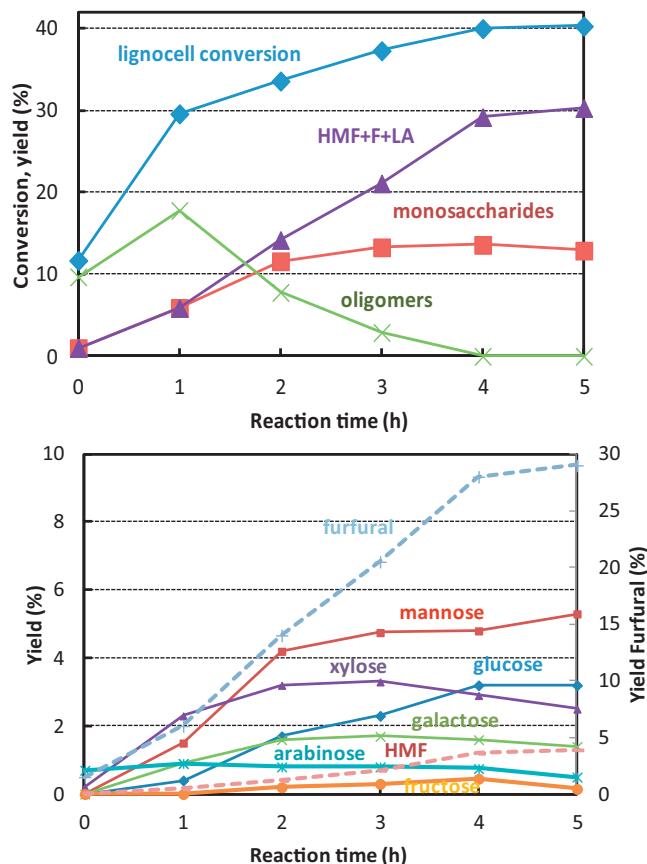


Fig. 1. Top: Lignocellulose conversion, and weight yield to the various products in relation to time. Bottom: Yield to monosaccharides (solid lines) and to degradation compounds (dotted lines) in relation to reaction time. Catalyst Zr/P/O. Reaction conditions: T 150 °C, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL.

rides was close to zero. After 1 h, the overall selectivity to sugars (monosaccharides and oligomers) was 80%, for 30% biomass conversion. In increased reaction times, a rapid decline of oligomer yield was observed, with a concomitant increase in both decomposition products (mainly furfural, as shown in Fig. 1, bottom), and all monosaccharides. Among the latter, the sugars showing the fastest increase were those obtained from hemicelluloses hydrolysis, i.e. arabinose (the only one showing a yield clearly higher than zero at nil conversion, being immediately dissolved), xylose, and galactose; conversely, a continuous increase in yield to both mannose and glucose (max yield 3.1%) was seen. Galactose, xylose, and arabinose showed a maximum yield after about 3–4 h reaction time. In these conditions, the overall selectivity to monosaccharides was just 29%, with 71% selectivity to degradation products. As for the latter, furfural was by far the prevailing product; its yield grew rapidly, and became 30% after 5 h reaction time, whereas the final yield to HMF was less than 2%. After 3 h reaction time, the yield to oligomers was nil, and decomposition products showed the fastest rise (furfural, however, with a low formation of HMF also, and no levulinic acid); at the same time all sugars (with the exception of the more stable glucose and mannose) underwent a subsequent decomposition. Worthy of note, in these conditions the mass balance was good (within the experimental error for the determination of biomass conversion), and the solution was still clear, showing that negligible further degradation compounds (e.g. humins) formed under these conditions. We would also like to point out that the distribution of monosaccharides obtained after 5 h reaction time was quite similar to that obtained with the diluted sulfuric acid at 36% biomass conversion (distribution with the sulfuric acid: 5% arabinose, 41% mannose, 22% glucose; 32% galactose and xylose).

The behavior of the Amberlyst 15 was similar to that shown by the Zr/P/O catalyst, albeit with some important differences (Fig. 2). Amberlyst was not more active in biomass dissolution and hydrolysis than Zr/P/O; in fact, the trend of conversion in relation to time was similar to that shown by the latter catalyst (indeed, the maximum conversion reached was the highest with the Zr/P/O catalyst). However, Amberlyst was more active in oligomer hydrolysis, as shown by both the rapid decline of the corresponding yield (already after 1 h reaction time, the yield to oligomers was negligible) and the concomitant increase in monosaccharide and decomposition product yield. In fact, the maximum yield to sugars (approx. 13%) was obtained after 1 h reaction only, whereas with Zr/P/O it took 3 h to reach the corresponding maximum yield (12.9%).

With Amberlyst too, the yield to monosaccharides and decomposition compounds was very similar at the beginning of the reaction time, but then the latter became the prevailing products. The highest yield to monosaccharides was obtained after 1 h only, and then a slight decline was observed for longer reaction times. For times longer than 3 h, the yield to HMF + furfural + levulinic acid also decreased, probably because of the formation of other, undetected decomposition by-products. The detailed distribution of products showed a major difference as compared to that shown by the Zr/P/O catalyst: the only sugar showing an increasing yield over the entire range of reaction time was glucose (max yield 4% after 5 h). Mannose still remained the prevailing monosaccharide, but the yield decreased notably for reaction times longer than 1 h. An important difference between the two catalysts concerns the yield to each decomposition compound; in fact, the yield to HMF was less than 0.3%, and the maximum yield to furfural was 27% (after 2 h reaction time). On the other hand, there was a non-negligible formation of levulinic acid (that conversely was not formed at all with the Zr/P/O catalyst), and of other unidentified decomposition compounds, while the formation of all the degradation compounds occurred more rapidly than with the Zr/P/O catalyst.

As for the comparison with the diluted H_2SO_4 treatment, in literature it is reported that, depending on reaction conditions, it is

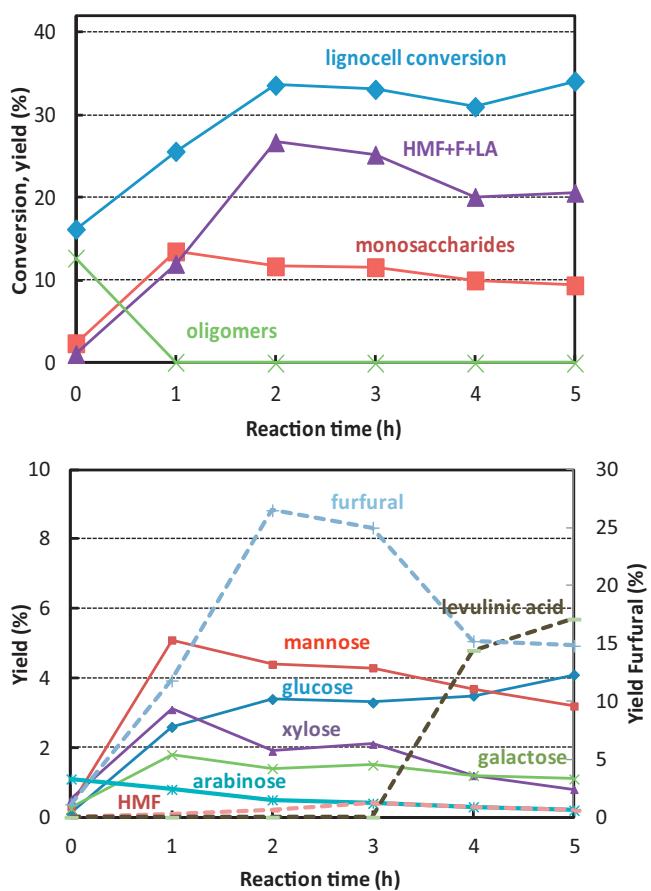


Fig. 2. Top: Lignocellulose conversion, and weight yield to the various products in relation to time. Bottom: Yield to monosaccharides (solid lines) and to degradation compounds (dotted lines) in relation to reaction time. Catalyst Amberlyst 15. Reaction conditions: T 150 °C, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL R.

possible to obtain from 20 to 60% of the theoretical yield to glucose in softwood pretreatment, by using diluted sulfuric acid [69]. Much lower yields are reported in [64], lower than 20% of the theoretical maximum yield to monosaccharides from cellulose, while using various diluted inorganic acids. With the softwood used in the present work, for a 45% cellulose content in the biomass, the yield to glucose corresponds to about 7% of the theoretical value with the Zr/P/O, and to 9% with the diluted sulfuric acid.

Overall, the Zr/P/O and the Amberlyst 15 catalysts showed a similar behavior, the major difference being both the affinity with oligomers and the activity in the formation of consecutive decomposition products. A similar yield to monosaccharides (and specifically to glucose) was observed with these two catalysts, although the latter was achieved in different reaction times. Moreover, the Zr/P/O system was less efficient than the diluted sulfuric acid (which is also the case for all the heterogeneous systems described in literature), but could be used as an alternative to the latter for the pretreatment of the biomass, especially when the saccharide fractions from hemicelluloses are not aimed at fermentation, but at a degradation to furfural.

We also studied the effect of a mechanical pretreatment of the biomass; the results obtained with and without the ball-milling treatment, after 3 h reaction time at 150 °C, are shown in Fig. 3. A moderate mechanical treatment of 20 h led to a slight increase in the biomass conversion, with a corresponding increase in yield both to monosaccharides and to decomposition products. The most noticeable effect, as expected, was seen on the yield of glucose (Fig. 3, bottom). This preliminary result indicates that the ball-

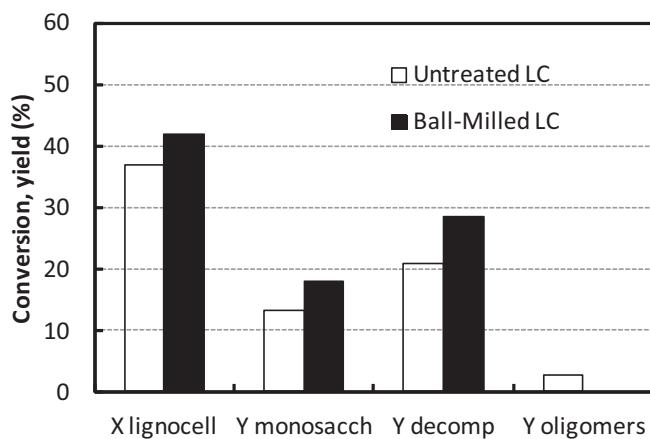


Fig. 3. Top: Lignocellulose conversion and yields to the products for the untreated and the ball-milled lignocellulose. Bottom: Yield to the monosaccharides. Catalyst Zr/P/O. Reaction conditions: T 150 °C, reaction time 3 h, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL. Ball-milling time: 20 h.

milling may have a positive effect on the biomass dissolution, thus improving the interaction between the solid catalyst and the biomass; however, this also enhanced the rate of degradation of sugars.

Final experiments were aimed at checking the possibility of recovery and reuse of the catalyst; with regard to this, among the various catalysts shown in Table 1, the Zr/P/O system was the one which could be more easily recovered and separated from the unconverted solid, because it showed a quicker sedimentation in water as compared to the biomass. Indeed, the extent of recovery was approximately 75–80% only if compared to the original weight; therefore, in order to examine the catalyst reusability, we used catalysts coming from parallel tests conducted under the same experimental conditions. Fig. 4 shows the result of the catalyst reuse experiments, for three sequential experiments. Before reuse, the spent catalyst was thermally treated at 400 °C for 10 h in air; such a long time was necessary in order to obtain the original white color of the catalyst. Data reported in Fig. 4 show that deactivation occurred after the first experiment, whereas the decline in conversion was less important for the third test than for the second one. The decline in activity also led to a decrease in the yield to monosaccharides and to a corresponding increased yield to decomposition compounds.

3.3. The hydrolysis of untreated and ball-milled microcrystalline cellulose (Avicel PH101)

In order to figure out how the Zr/P/O catalyst was positioned as compared to the best system described in literature, we con-

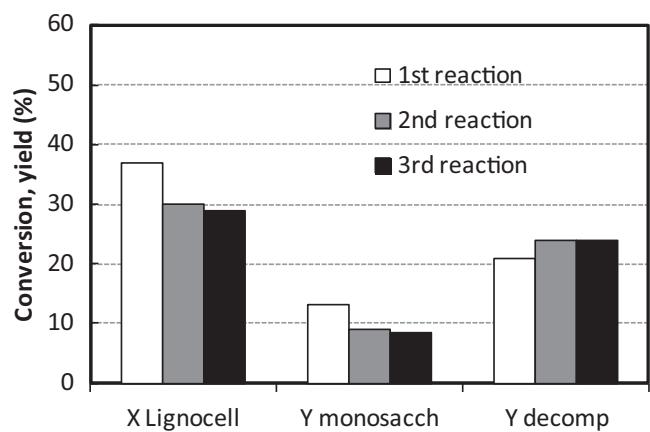


Fig. 4. Lignocellulose conversion (X Lignocell) and yield (Y) to monosaccharides and to decomposition compounds in relation to the fresh Zr/P/O catalyst, and for the recovered and regenerated catalyst. Reaction conditions: T 150 °C, reaction time 3 h, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL.

ducted hydrolysis experiments using microcrystalline cellulose, Avicel PH101. Various reviews compare the catalytic performance obtained with several systems, both homogeneous and heterogeneous [25,26,29].

With regard to the hydrolysis of the untreated cellulose, the best glucose yield reported in the literature so far was obtained with SO₃H-bearing amorphous carbon, prepared by the partial carbonization of cellulose followed by sulfonation. In 6 h reaction time at a temperature of 100 °C, by using a catalyst-to-cellulose weight ratio of 12, a glucose yield of 4% was reported, the major products being water-soluble β-1,4 glucans (64%) [46–48]; worthy of note, at these low-T conditions most conventional and non-conventional solid acids (e.g. Amberlyst 15, Niobic acid and Nafion NR-50) gave no conversion of cellulose at all. On the other hand, much better yields were obtained starting from ball-milled cellulose; for example, in the case of sulfonated activated carbon, a 41% glucose yield was obtained at 150 °C, 24 h reaction time, on decrystallized cellulose, with a catalyst/cellulose wt ratio of 1 [43–45]. Under quite similar conditions, a 50% yield of glucose was achieved by using sulfonated silica-carbon nanocomposites [52]. A similar result was also obtained in 3 h reaction time, at 150 °C, with sulfonated SBA-15 [51]. An outstanding yield of 75% (with high selectivity to glucose) was obtained by using sulfonated mesoporous carbon CMK-3, again at 150 °C with a reaction time of 24 h [50].

Fig. 5 shows both the conversion of the untreated microcrystalline cellulose and the yields to monosaccharides in relation to the reaction time at 150 °C, whereas Fig. 6 reports the results obtained at 200 °C. In the former case, it is shown that after 10 h reaction time, the yield to monosaccharides (which only consisted of glucose, with non-detectable amounts of both fructose and mannose) was 5.8%, with a 19% cellulose conversion and, quite remarkably, no formation of decomposition compounds; worthy of note, a glucose yield of 5.8% is the best value ever reported in literature for a heterogeneous acid catalyst on an untreated microcrystalline cellulose. Even after a prolonged reaction of 24 h, the yield to HMF was still very low, but the glucose yield was only 6.4%. Table 2 compares the cellulose conversion and yield to glucose of the Zr/P/O catalyst with that obtained with other reference solid acids (H-Mordenite with SAR ratio of 15, and Amberlyst 15), with corresponding results obtained with diluted sulfuric acid and 2-naphthalenesulfonic acid. The yield to glucose obtained with sulfuric acid (which also gave a 1.8% yield to decomposition compounds) was similar to that shown by the Zr/P/O catalyst; conversely, a better yield to glucose (over 10%) was obtained with the homogeneous catalyst 2-NFA (which also gave a 2.1% yield to decomposition compounds) [70].

Experiments carried out at 200 °C led to a rather remarkable, unprecedented 21% glucose yield after 2 h reaction time; however, longer reaction times led to a drastic fall in the glucose yield. The maximum cellulose conversion achieved was 70%, after 3 h reaction time. The yield to furfural showed a similar trend, with the top reached after 1 h reaction time; after 2 h reaction time the yield to levulinic acid increased rapidly, whereas that to HMF remained very low during the entire experiment time. It may be concluded that in such hard reaction conditions further degradation compounds became the largely prevailing products after 2 h reaction time, as is also apparent from the brownish color of the hydrolysate

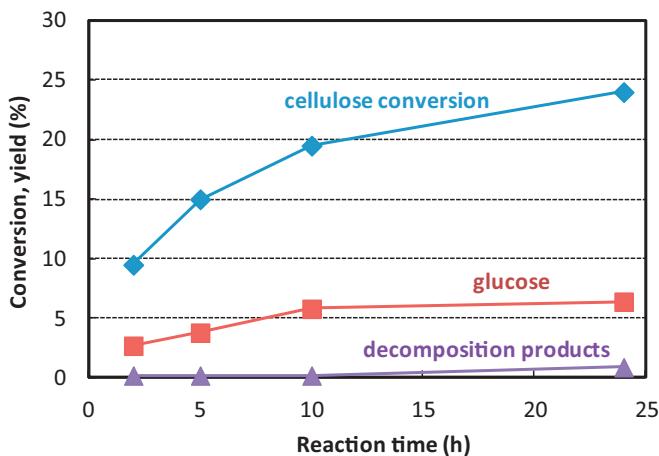


Fig. 5. Conversion of untreated cellulose and yield to glucose and to decomposition compounds (HMF) in relation to time. Catalyst Zr/P/O. Reaction conditions: T 150 °C, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL.

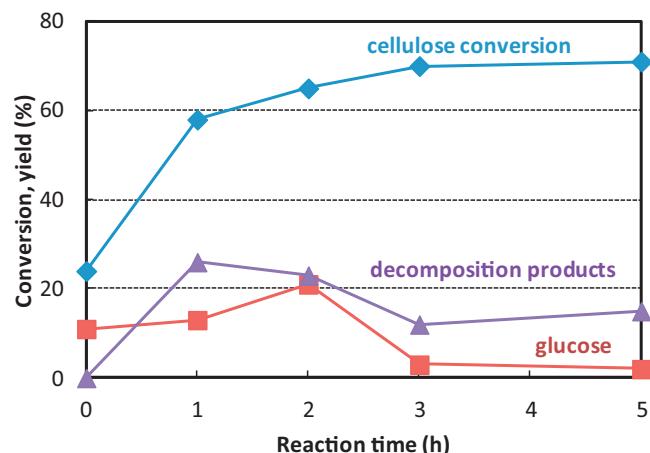


Fig. 6. Conversion of untreated cellulose and yield to glucose and to decomposition compounds (HMF + F + LA) in relation to time. Catalyst Zr/P/O. Reaction conditions: T 200 °C, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL.

Table 2
Comparison of some heterogeneous and homogeneous catalyst behaviors in the hydrolysis of untreated Avicel PH101.

Catalyst	T (°C), t (h)	Cellulose conversion (%)	Monosacch. yield (%)
Autohydrolysis	150, 5	6	0.6
Zr/P/O	150, 10	20	5.8
H-mordenite	150, 5	21	2.5
Dil H ₂ SO ₄ (pH 1.6)	160, 2.2	16	5
2-NFA (1 wt%)	160, 2.2	23	10.6

2-NFA: 2-naphthalenesulfonic acid.

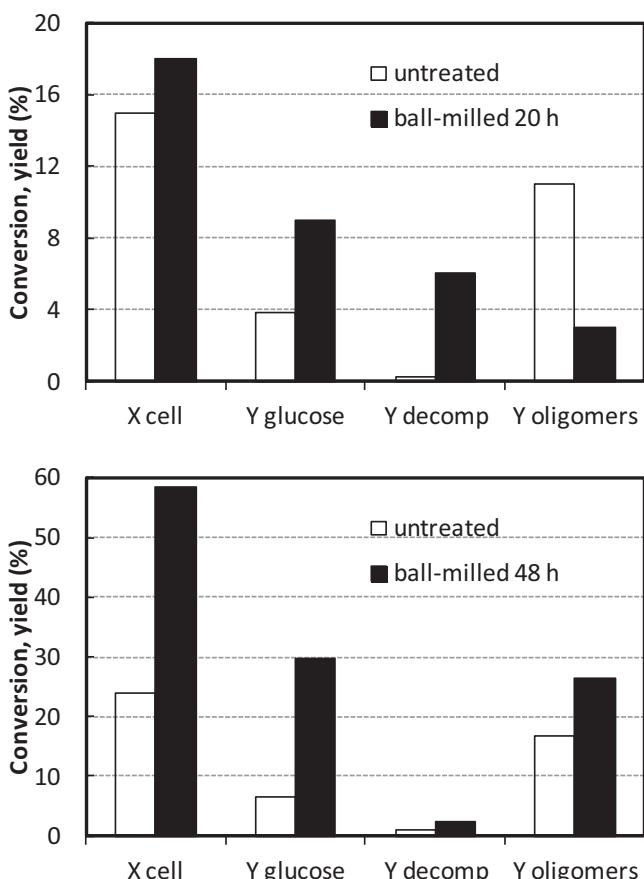


Fig. 7. Comparison of crystalline cellulose conversion and yield to glucose and decomposition compounds for the untreated cellulose and for the ball-milled cellulose. Top: Ball-milling 20 h; reaction conditions: T 150 °C, reaction time 5 h, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL. Bottom: Ball-milling 48 h; reaction conditions: T 150 °C, reaction time 24 h, biomass weight 2.5 g, catalyst weight 2.5 g, water 50 mL.

solution. Moreover, the residual unconverted cellulose appeared to be coked after such treatment at high temperature.

We then treated the microcrystalline cellulose with ball milling, for either 20 h or 48 h. Fig. 7 (top) compares the catalytic behavior after 20 h ball-milling time with that starting from untreated cellulose, for a 5 h reaction time (T 150 °C), whereas Fig. 7 (bottom) shows the comparison of conversion and yield achieved after 24 h reaction time (T 150 °C), for both the untreated cellulose and the cellulose after 48 h ball-milling pretreatment. It is shown that the mechanical comminution led to an increased cellulose conversion, which was quite considerable in the case of cellulose ball-milled for longer time. In the former case, the treatment slightly affected cellulose conversion, but led to a considerable change in the product distribution. In fact, the yield to both glucose and degradation compounds increased greatly starting from the ball-milled cellulose; the mass balance in the latter case was close to 100%, which indicates that the cello-oligomers were more efficiently transformed into consecutive products with the ball-milled cellulose. This means that the ball-milling treatment improved the accessibility of acid sites to the substrate, with a more efficient hydrolysis of glucans at the expense of a simple solubilization effect. The effect of an increased glucose yield was much more marked when the mechanical treatment was carried out for 48 h, as shown in Fig. 7 (bottom). An outstanding 30% yield to glucose was registered, yield to HMF being 2.4%, for a 59% cellulose conversion.

Comparing the results obtained in cellulose hydrolysis and literature data makes it possible to draw some conclusions. It is known

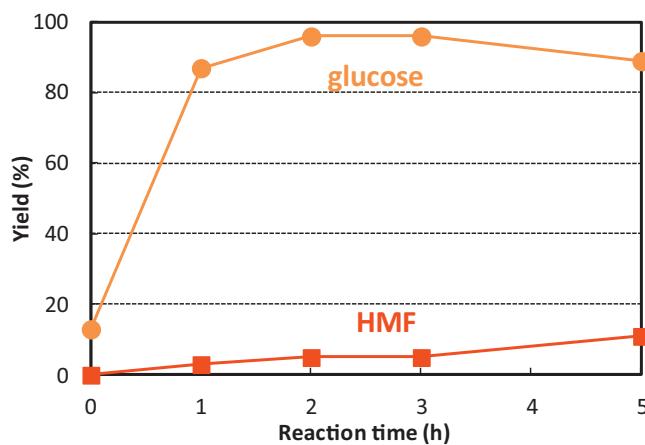


Fig. 8. Glucose and HMF yields in relation to time in cellobiose conversion. Catalyst Zr/P/O. Reaction conditions: T 150 °C, cellobiose 1.5 g, catalyst 1.5 g, water 30 mL.

from the literature that in order to be efficient in cellulose hydrolysis, solid acids must be able to adsorb β -1,4-glucans on the surface and interact with them by means of, for example, acid OH groups [46,47], which make it possible to decrease the activation energy for the hydrolysis reaction; the interaction can also be promoted by the presence of surface Lewis acid sites [71]. We conducted further experiments on cellobiose hydrolysis, the shortest glucan in which two glucose molecules are linked by a β -1,4-glycosidic bond, with the aim of investigating the ability of the Zr/P/O catalyst to interact with glucans. Kitano et al. [47] compared the rate of cellobiose hydrolysis for several catalysts, including their system prepared by the sulfonation of amorphous carbon; the latter achieved a glucose yield exceeding 70% after 9 h at 90 °C, while the plateau in the conversion was reached after 10 h, with total selectivity to glucose.

Fig. 8 reports the results of kinetic experiments carried out with cellobiose as the hydrolyzable substrate, at 150 °C; the autohydrolysis gave 6.9% and 52% yield after 1 h and 3 h, respectively. After 2 h reaction time the catalyzed cellobiose conversion was completed, the corresponding yield to glucose being 97%, and the yield to HMF 3%. Total selectivity to glucose was obtained at 100 °C, but after 3 h reaction time cellobiose conversion was only 6%. Compared to literature data, the glucose productivity obtained at 100 °C with our Zr/P/O catalyst ($0.03 \text{ g}_{\text{glucose}} \text{ h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$) was lower than that reported for the most active sulfonated amorphous carbon ($0.08 \text{ g}_{\text{glucose}} \text{ h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$) [47], but it was as high as $0.9 \text{ g}_{\text{glucose}} \text{ h}^{-1} \text{ g}_{\text{catalyst}}^{-1}$ at 150 °C.

3.4. The problem of P leaching from the Zr/P/O catalyst

It is now recognized that one main problem in catalysts bearing $-\text{SO}_3\text{H}$ groups for cellulose hydrolysis is the leaching of active sites, even though this aspect has only been marginally considered in literature. The experiments in Fig. 4 demonstrated that our Zr/P/O catalyst also showed an initial decline in activity between the first and the second experiment. Therefore we conducted a detailed investigation into the reasons for this behavior by performing the following selected experiments.

We first treated the Zr/P/O catalyst under the same experimental conditions used for hydrolysis experiments (150 °C, 5 h), but in the absence of cellulose. Under these conditions, some of the P dissolved in the aqueous medium (400 ppm of P, as determined by means of the XRF analysis of the solution), and correspondingly the P/Zr atomic ratio decreased from the original value of 1.9 ± 0.1 , to 1.6 ± 0.1 . There was no dissolution of Zr at all. This indicates that the calcined catalyst contained a certain fraction of the P which was "free", i.e. present in the form of either soluble polyphosphoric

Table 3

Results of experiments carried out with the recovered and reused Zr/P/O catalyst, and with hydrolysate.

Exp. No.	Catalyst, reaction time	Cellulose conversion (%)	Glucose yield (%)
1	Fresh Zr/P/O, 3 h	13.8	4.1
2	Fresh Zr/P/O, 24 h	24.0	6.4
3	Used Zr/P/O, 3 h	5.0	2.4
4	Used Zr/P/O, 24 h	25.0	8.1
5	No catalyst, reaction of the hydrolysate (pH 3.0) after exp. 1, 3 h	10.5	2.2
6	No catalyst, reaction of the hydrolysate (pH 3.0) after exp. 1, 24 h	24.0	4.0

Reaction conditions: T 150 °C, catalyst (exp. No. 1–4) 1.5 g, untreated cellulose (exp. No. 1–6) 1.5 g, water 30 mL.

acid, or ammonium (hydrogen) phosphate. The latter hypothesis is more likely, because the pH of the aqueous solution after the hot-dissolution treatment was close to 5, whereas the dissolution of phosphoric acid in water using exactly the same P concentration as that determined in the filtered solution led to a pH lower than 2.0. This indicates that, even after thermal treatment at 400 °C, the composition of the catalyst is not that of a Zr phosphate, but rather that of a mixed ammonium Zr phosphate. We recorded an IR spectrum of the calcined sample, and we confirmed the hypothesis of the presence of ammonium ion (typical absorption band at ca 1440 cm^{-1}); the intensity of this band decreased remarkably after the dissolution treatment, and after reaction as well. A similar amount of P (between 300 and 400 ppm, depending on the experiment type) was also found in the hydrolysate solution after the first reaction (using the fresh catalyst) with both crystalline cellulose and lignocellulose; it is also worth noting that the pH of the hydrolysate after these reactions was close to 3.0.

We also carried out the recovery and reuse of the catalyst after the reaction with untreated cellulose. In this case, however, the recovery of the used catalyst was more difficult than it was with the lignocellulose, since the sedimentation rate difference between the catalyst and the cellulose was not such as to allow an easy separation between the two types of solid particles. Therefore, in this case, we burned the unconverted cellulose by means of a prolonged treatment in air (400 °C for 15 h); the cellulose-free regenerated catalyst was then reused for a further reactivity test. The used and regenerated catalyst showed a reduced surface area (from the initial $108 \text{ m}^2/\text{g}$ to $65 \text{ m}^2/\text{g}$), and a reduction in the P/Zr atomic ratio similar to that shown after the dissolution treatment in water only. We also took the hydrolysate from a standard experiment, and produced a reaction by adding fresh cellulose (that is, in the absence of the Zr/P/O catalyst). Table 3 compares the cellulose conversion and the yield to sugars in the various experiments conducted. The reported experiments demonstrate that the pH of the hydrolysate (pH 3.0) was low enough to cause further cellulose hydrolysis, whereas the obtained yield to sugars was lower than that obtained in the presence of the Zr/P/O catalyst (both with the fresh and the used ones); this acidity, however, was not due to the dissolved P (as reported above), but probably to soluble organic compounds derived from sugar decomposition. The used catalyst showed a somewhat surprising behavior; after 3 h reaction, the sample gave a lower cellulose conversion than the fresh one (although with better selectivity to glucose), as was also the case with lignocellulose (Fig. 4). After 24 h reaction time, however, the yield to glucose was slightly better than that of the fresh catalyst.

It may be concluded that the loss of P from the fresh catalyst led to some changes in the main catalyst characteristics, among which the most important was a reduced surface area. These changes might be the reason for the lower lignocellulose and

cellulose conversion experimentally observed after 3 h reaction time and the slightly different distribution of products. However, in the long-term experiment, under conditions at which the conversion reached a plateau, the used catalyst showed no marked differences in the hydrolysis of oligomers as compared to the fresh catalyst. Moreover, our results demonstrate that the P released during the first use did not contribute to the catalytic behavior experimentally observed for the fresh Zr/P/O catalyst.

4. Conclusions

In this paper we compared the reactivity of several heterogeneous catalysts in the hydrolysis of a softwood sawdust. A Zr phosphate catalyst showed an interesting behavior, with a relatively high yield to monosaccharides, comparable to that achieved with Amberlyst 15, but still lower than that obtained with the conventional diluted sulfuric acid treatment. Furthermore, the Zr/P/O system could also be separated from the unconverted biomass, and reused after regeneration; it showed a decline in both activity and monosaccharide selectivity during the first reuse, but afterwards its behavior remained more stable. The hydrolysis of an untreated Avicel PH101 at 150 °C also gave a 5.8% yield to glucose with nil formation of decomposition products; at 200 °C, an outstanding 21% yield to glucose was obtained, albeit with a significant formation of degradation compounds. The hydrolysis of the ball-milled cellulose gave 30% yield to glucose, a 59% cellulose conversion, and a 2.4% HMF yield. The Zr/P/O catalyst was also very active in cellobiose hydrolysis, with a 97% yield to glucose achieved at 150 °C after 2 h reaction time. The effect of catalyst stability was also investigated; it was found that both the initial loss of P and the reduced surface area were responsible for the experimentally observed reduced activity of the catalyst during the first catalyst reuse in both lignocellulose and cellulose hydrolysis.

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